# MDI and TDI: Safety, Health and the Environment.

## A Source Book and Practical Guide


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# Contents

# MDI and TDI usage: responsible risk management

Methylenediphenyl diisocyanate (MDI) and toluene diisocyanate (TDI) are the most important commercial products in the family of organic chemicals having two or more isocyanate groups in the molecule. MDI and TDI are produced in very large chemical plants and are transported to users in various ways, ranging from delivery of a single drum through to bulk delivery in a ship's tank. These diisocyanates are then used in a wide diversity of processes to produce an almost endless range of polyurethane and other products. Approximately a quarter of a million workers are involved in the global polyurethane manufacturing industry. This book is about the safety, health and environmental problems that may arise during the handling of MDI and TDI, and how to prevent them. The authors have drawn upon many years of industrial experience throughout the world to describe what is generally believed to be *best practice*.

This introductory text is about:

- ways of defining problems using the concepts of exposure, hazard and risk;
- a framework for working safely with these chemicals, and for sharing effective solutions throughout the industry by applying the practices of product stewardship.

## Exposure, hazard and risk

Throughout the book the terms exposure, hazard and risk are considered in relation to the impact of MDI or TDI on humans (the workforce or the community) or on the environment.

The extent, duration and route of *exposure* determines a dose (amount taken in per mammal or other species over a time period). In some situations, concentration can be monitored and exposure cited as a concentration of the substance in question. Where monitoring is not feasible exposure scenario models can be used which are based on the properties of the diisocyanate and on reasonable assumptions about handling during manufacturing and technical use (by workers), general use (by consumers) and from releases as affecting the community and the environment.

The *hazard* of a chemical is an intrinsic property, just like colour, odour or melting point. It can be determined from appropriate experiments (toxicity studies) and from experience following human exposure (epidemiology, case studies, clinical experience). The dose or exposure level at which no adverse health effects are seen is the NOAEL (No Observed Adverse Effect Level). If there is insufficient information available for the exposure or the hazard to be defined, worst case estimates can be made to generate preliminary product safety evaluations.

*Risk* can be described by a simplified equation demonstrating that both hazard and exposure are directly related to risk:

$$\text{hazard} \times \text{exposure} = \text{risk}$$

The above expression cannot describe the diverse reactions of chemicals with humans and the environment, and is a great simplification of what are, almost invariably, complex situations, often under constantly changing circumstances. However, it is very useful in understanding risk, and especially risk management. Since hazard is an intrinsic, unchanging property of the chemical, then the only way to reduce risk is to reduce exposure. When there is no exposure, there is no risk. *No exposure* may, of course, imply *no usage* and hence no benefit to society. In some cases, the benefits outweigh the risk and at other times, the risks may be unacceptable compared to the benefits, and risk management methods must be explored.

*Hazard × exposure = risk*
This expression can be used as a guide to risk only in some cases. One obvious limitation is that it cannot be used with threshold concentrations of toxic agents. The relationship would be expressed better in the mathematical form

risk = function (exposure, hazard)
or
risk = function (exposure, toxicity)

For humans, depending on the type of adverse health effect, risk can be expressed as the number of cases over background in a population; for example, for cancer: 1 in 1 000 000 ($10^6$). For other adverse health effects, or as an alternative to the above expression, it is common practice to compare the dose for exposed humans with doses extrapolated from animal studies which include safety factors at which no adverse effect is seen (the *margin of safety* approach). Community exposure limits based on risk assessment principles have been developed by the US Federal and State authorities as a practical means of setting a basis for regulatory limits.

In the case of the environment, the following are recognized:

- effects on biological organisms, for example fish, crustacea, algae and bacteria;
- effects on soil, water and air.

A further way of assessing risk, which can be used in environmental situations, is to compare an exposure concentration with a concentration which is known not to produce a defined adverse effect in a given species. Such an effect might be lethality. A regulatory approach to risk encompassing this broad philosophy, such as that used in the European Union, is illustrated in *Part 4, The environment*. In this approach, the ratio

$$\frac{\text{predicted exposure concentration (PEC)}}{\text{predicted no-effect concentration (PNEC)}}$$

is used as a criterion for the acceptability of the concentration of discharges to the environment. Where the ratio is greater than one, environmental damage may occur and risk management should be considered.

It is always preferable to prevent releases of diisocyanates, than to deal with the effects of the releases, however competently this is done. *Part 2* of this book is particularly concerned with the issues involved in reducing exposure at source by good working practices in the polyurethane industry and by appropriate design of equipment for the transport and handling of diisocyanates.

## Risk management scenarios for MDI and TDI

In this section the ways of distributing and using MDI and TDI are described in order to examine how exposure may potentially occur. Each situation presents its own challenges and demands its own approaches to risk management.

The continuous plants in which diisocyanates are manufactured employ few people. However, many more people are employed at workplaces where the diisocyanates are used to manufacture polyurethanes (Table 1). In Europe alone, about 72 000 people work in 6000 facilities making polyurethanes. An important aspect of this book is, therefore, the safe handling of diisocyanates in these workplaces. Safe transport of diisocyanates from manufacturing plants to the sites of polyurethane production, and their safe storage once delivered, are essential.

***Table 1*** **MDI, TDI and polyurethane production in Europe (1998).**

| | |
|---|---|
| **MDI and TDI production** | |
| MDI and TDI producers | 9 |
| Numbers employed | 1000 |
| **Polyurethane production** | |
| Polyurethane producers | 6000 |
| Numbers employed | 72 000 |

Based on ISOPA (1999) and III information.

## *MDI and TDI production plants*

MDI and TDI are produced in relatively few manufacturing plants. The capacities of the manufacturing plants are in the range of 10 000 to 150 000 tonnes per annum, with an average size of about 100 000 tonnes (about 200 million pounds) per annum. These plants are usually sited in very large chemical production complexes in which the feedstock is often also produced (see Figure). MDI and TDI are produced in essentially closed systems, with highly sophisticated control and safety arrangements, each plant requiring only a small number of operatives.

**MDI manufacturing plant (figure by courtesy of Huntsman Polyurethanes)**

There are no releases of MDI or TDI to water or soil under normal operating conditions. Normal releases to atmosphere from manufacturing sites are at very low concentrations only, which give extremely low levels indeed outside the sites. Further, any releases of airborne MDI or TDI are degraded in air to harmless final products. MDI and TDI manufacturing complexes are subject to highly prescribed and rigorous regulations and safety procedures to comply with international, national and local standards; these deal with both normal manufacturing and accident scenarios. Production plant operators undergo lengthy training that is tailored to the specific sites. The site safety procedures are in conformity not only with regulations but also with the safety philosophies of individual manufacturing companies. These activities are beyond the scope of this book. See *Part 5.1* for an outline of the chemistry of the manufacture of MDI and TDI.

### Transport

There are distribution systems from the plants manufacturing MDI and TDI using a variety of modes of transport, to allow the materials to be delivered to the thousands of diverse types of polyurethane manufacturing sites. The sizes of consignments of MDI and TDI vary from as little as two litres to as much as one million litres. Drums and intermediate bulk containers (IBCs) are transported by normal trucks or freight containers. Bulk shipments are made by dedicated temperature-controlled road tankers, by rail cars or by ship in even larger quantities. No losses whatever are expected from these closed systems under normal transportation conditions.

Records indicate that accidental spillage during the transportation of MDI and TDI is very infrequent and rarely of major impact (see *Part 4, The environment* for more details). When incidents do involve the spillage of MDI or TDI, the effects can extend to:

- the environment;
- the workforce (transportation personnel and emergency service personnel);
- the community.

### The workplace

The processing plants for the production of polyurethanes or other MDI- or TDI-based products are the workplaces that will be dealt with primarily in this text. Workplaces also include *systems houses* (facilities for the preparation of specialised diisocyanate formulations) and all storage areas for the diisocyanates. The workplace may be indoors in a factory, or in the open air, as in the case of spraying on construction sites or when applying running track compounds. Releases of MDI or TDI may affect:

- the workforce;
- the environment within the site.

*Part 2, Handling MDI and TDI* deals with many of the practical issues involved in the management of risks in workplaces. Exposure reduction can be achieved in a wide diversity of ways, including modifying production processes, improving ventilation design, removing releases from exhaust air, and improving training and communications. In those situations where releases cannot be controlled at source, careful choice of personal protective equipment will be necessary. *Part 3, Health* and *Part 4, The environment* review the scientific knowledge relevant to the effects of MDI and TDI on human health and on the environment.

### *Releases from polyurethane sites*

Airborne releases at low concentrations may occur during normal, regulated processing of MDI or TDI. These releases may affect:

- the workforce;
- the community;
- the environment outside the site.

People in the workforce and the community in the neighbourhood of the site differ significantly as regards the potential health effects of exposures to chemicals. The workforce is usually a healthy selected group, which should be well educated about the effects of the chemicals to which they may be exposed in the workplace. The community is not selected as regards health or age, and individuals may be ignorant of the health effects of these substances. The workforce is exposed for a limited period as regards daily and lifetime exposure. Members of the community may be exposed for an entire lifetime, albeit usually at extremely low levels. The workforce should be subject to medical surveillance. The community would be subject to such scrutiny only in very exceptional situations. Hence, regulations covering releases reflect the differences between a workforce and the general community. Control of releases from polyurethane manufacturing plants is discussed in *Part 2*.

MDI and TDI should not be disposed of by discarding them into soil or into drains. However, in the case of an accident, soil or drains may possibly become contaminated. Even in the event of an accidental spillage, the diisocyanates would not be expected to migrate from the site through soil because of their physical and chemical properties (see *Part 4, The environment*). Whilst MDI or TDI might, theoretically, flow from the site via drains, sites on which chemicals are used should be designed to ensure that this is not possible.

## Responsible Care®: a framework for industry action

Responsible Care contains six codes of management practices:

- community awareness and emergency response code;
- pollution prevention code;
- process safety code;
- distribution code;
- employee health and safety code;
- product stewardship code.

The recognition by industry of the need for responsible risk management of chemicals led it to establish the principles of *Responsible Care*. Responsible Care is a set of voluntary initiatives based on the principles of autonomous decision-making and individual responsibility. Under Responsible Care, companies engaged in the manufacture or handling of chemicals make public commitments in their management practices.

*Product stewardship* is a set of activities within Responsible Care aimed at protecting the environment and ensuring safety at all stages of the life cycles of chemical substances, from development and manufacturing through distribution and use, to final consumption and disposal (in other words, the cradle-to-grave approach).

Whilst everyone can be considered as a steward of health and the environment, those associated with the handling of chemicals have additional responsibilities and opportunities to fulfil that role. Product stewardship provides a clear framework for the handling of diisocyanates and for influencing others to work in a responsible way. It is not an activity just for the original chemical company that produces diisocyanates, but extends to everyone who processes or in some way uses MDI or TDI, and includes relevant safety training and communication of health and environmental information. Effective product stewardship programmes also address issues connected with the public's concerns about chemicals, so that there can be meaningful and effective collaboration with the community, to the advantage of all.

## Product stewardship and regulations

Those handling MDI or TDI will need to observe regulations, whether international, national or local. Information given in this book should not be used in conflict with any legislation. However, regulations often cover a range of chemicals or situations and may be of limited use in ensuring the safe handling of specific chemicals in all situations, because it is possible to comply fully with regulations and still allow avoidable risks to occur. The aim of product stewards should be to minimize possible adverse effects of all chemicals by the best available practical means. The approaches to the protection of human health and the environment, as described in this book, fulfil the requirements of product stewardship.

In this book the need for product stewardship has been emphasized, as an informed, responsible way of protecting human health and the environment. This approach, consistently and diligently applied, will complement and frequently extend beyond the requirements of regulations. For example, a diisocyanate supplier may decide to refuse to sell a product to a polymer producer who consistently ignores the regulations, or who does not observe safe working practices despite being given relevant information.

Increasingly, regulatory authorities worldwide are preparing inventories of chemicals which are sold commercially. The main purpose of these inventories is to enable data to be collected on substances that are sold in large quantities, or that are believed to be particularly hazardous. The end results of this work are the assessments of risks to human health and to the environment from the production, transport and use of the chemicals. These assessments are followed by risk management activities, as necessary. It is in the interests of the government agencies involved, the producers of the chemicals and the general public that valid data and interpretations of risks are produced. Producers of MDI and TDI see these activities as important aspects of their product stewardship commitments. Two examples of cooperative work between government agencies and the manufacturers of MDI and TDI are summarized below. Without the willing cooperation of both regulators and industry, much less progress would have been made, possibly leading to the adoption of over-cautious assessments of potential risks, unnecessary regulation, excessive costs and constraints to beneficial industrial activity.

## Case history 1

*Dr J D Walker, Director, TSCA Interagency Testing Committee, US Environmental Protection Agency*

Under the Toxic Substances Control Act (TSCA), 'it is the policy of the United States that adequate data should be developed with respect to the effect of chemical substances and mixtures on health and the environment and that the development of such data should be the responsibility of those who manufacture and those who process chemical substances and mixtures.' To implement this policy, the TSCA Interagency Testing Committee (ITC) considers chemical substances and mixtures for which adequate data should be developed and facilitates the submission of these data by recommending chemical substances and mixtures for health effects, environmental fate or ecological effects testing in May and November Reports to the Administrator of the US Environmental Protection Agency (http://www.epa.gov/opptintr/itc/). In 1995, as part of its then on-going evaluation of data needs for isocyanates, the ITC solicited data on the use of 10 isocyanates, including MDI and TDI. A dialogue group of government and industry representatives was organized to facilitate data retrieval. Cooperation between government and industry representatives resulted in the submission of data to meet government needs and the removal of isocyanates from the ITC's TSCA section 4(e) *Priority Testing List*. The ITC was able to obtain many previously unpublished data and learned that, in most applications, MDI and TDI are fully reacted in the polyurethane manufacturing processes. Industry, for its part, learned of the US Government's requirements for valid scientific data on the health and environmental effects of isocyanates. All the data submitted by industry are now in the public domain. Further information on the work of the ITC is available (Walker, 2000).

Information on tests that have been conducted to assess the health effects, environmental fate or ecological effects can be obtained from the generic internet addresses listed below. These sites should be searched for MDI or TDI or their Chemical Abstract Service Registry numbers:

a. Organization for Economic Cooperation and Development (OECD) Screening Information Data Set (SIDS): http://www.oecd.org/
b. Data summaries in response to the US EPA's High Production Volume chemical challenge programme: http://www.epa.gov/opptintr/
c. Unpublished health and safety studies in the public domain and indexed in the TSCA Test Submissions database: http://esc_plaza.syrres.com/ and in the Right to Know Network: http://www.rtk.net/

## Case history 2

In 1981 the European Union completed its *Existing Chemicals* inventory. Later it began its process of risk assessment of high production volume chemicals. MDI was included in the Third Priority List and in 1997 the Belgium Government was given the role of selecting an individual (the Rapporteur) to lead the risk assessment process.

The Belgian Rapporteur and his principal collaborator commenced the exercise by drawing together the key organizations and showing their intent to proceed in a friendly, collaborative spirit. Industry was represented by the European Isocyanate Producers Association (ISOPA), the Lead Company (an MDI manufacturer based in Belgium) and the III Scientific Office based in the UK. Although industry experts had already been involved in risk assessments of chemicals in the First and Second Priority Lists, MDI was the first chemical to be assessed by Belgium. The Rapporteur recognized that each side could make a significant contribution to the process. He and his agents would have the advantage of reviewing the hazards of MDI and the exposure scenarios without preconceived ideas. Industry could share its experience and knowledge of the scientific literature. Further, industry was already familiar with procedural aspects of such exercises and had assembled data in appropriate formats.

The exercise, within the framework of the EU Technical Guidance Document, commenced with the timetable and lines of communication being established. The scientific collaborators of the Rapporteur, based in the University of Leuven and the University of Liège, commenced their health and environment assessments using the International Uniform Chemicals Information Database (IUCLID) previously generated by industry. They liaised with industry representatives, which led to a mutually positive exchange of information and judgements. Visits to MDI and polyurethane production sites were arranged and these resolved many important questions on emissions, occupational hygiene and safety. The III Scientific Office played a fiduciary role in processing production and release statistics.

A crucial aspect of the process was the assessment of human exposure to MDI. This is largely associated with the user workplace, that is, with facilities making polyurethanes. Due to the excellent relationships fostered by ISOPA and III with the downstream polyurethane industry, considerable information on exposure was made available to the Rapporteur, even though the downstream industries were under no obligation to assist in the exercise.

There was seen to be no requirement for environmental risk management measures for MDI to be implemented. However, there are outstanding questions (2002) regarding the health assessment, which are being resolved as industry projects come to fruition.

## Structure of this book: Parts 1 to 5

The aim of the book is to serve those in the polyurethane industry involved in the practicalities of handling MDI or TDI, as well as those involved in supplying information or acting as consultants within or outside the industry. To achieve this, there is a broad hierarchy of information in this book from the simple to the complex. Key messages are repeated to allow sections to be read in isolation without the need for extensive cross-referencing.

## Part 1, MDI, TDI and the polyurethane industry

The various commercial forms of MDI and TDI are discussed, and the nomenclature and chemical structures of their component isomers described briefly. The wide usage of MDI and TDI in the manufacture of polyurethanes is outlined.

## Part 2, Handling MDI and TDI

This part is prefaced by an explanation of the need for comprehensive safety systems. *Part 2* covers a number of important concepts (*Key Themes*) with much detailed information, and gives relevant information on what are believed to be current best practices for the transport, storage and the handling of these diisocyanates in workplaces. The text of *Part 2* includes important practical messages from other parts of the book, especially on health care, so that it can be read in isolation from subsequent parts.

## Part 3, Health

This specialised text is intended for those who need a deeper insight into health effects than is given in *Part 2*. Health in the polyurethane industry is an extremely important issue. It is very well established that respiratory effects can be attributed to over-exposure to diisocyanates. This text deals with such effects and it also surveys the wide range of studies to investigate other possible health effects. Data from laboratory animal studies and their relationships to potential human effects are reviewed.

## Part 4, The environment

This is also a specialized text: it will be of interest particularly to chemists and environmental scientists. There is not a long and intense history of publication in the sphere of environmental science of diisocyanates as there is in the health sector. Accordingly, the opportunity has been taken to draw from all key studies, the majority of which have been completed over the last 15 years, and which have not yet been published widely.

## Part 5, Supporting sciences

These texts are largely for the expert and those involved in detailed regulatory submissions. The text on sampling and analysis is considered to be particularly important since analysis of MDI and TDI can be difficult, and meaningful analytical results are crucial to an understanding of health and environmental risks. The text draws upon the experience of professional analysts: such an array of important practical detail is not available in other texts. The fire behaviour of MDI and TDI is also reviewed in detail. Whilst their fire behaviour is unexceptional, a detailed text has been provided to describe the complexities of the combustion processes.

# Reading

## References cited in the text

ISOPA (1999). *Socio-economic Data on the European Polyurethanes Industry*, European Isocyanate Producers Association, Brussels.

Walker, J. D. (2000). ITC-Industry Isocyanate Dialogue Group data and information exchange. US Environmental Protection Agency. *III Report No. 11387*. Available from: British Library Document Supply Centre, Boston Spa, Wetherby, West Yorks.

## Further reading

Bastian, C. and Strobbe, G. (1996). Product stewardship polyurethanes. *Utech '96 – Processing Workshop 3: Flexible Slabstock Polyurethane Foams*, The Hague, 26–28 March, paper 5, Rapra Technology, Shrewsbury (ISBN 1-85957-102-6).

CCPA (1998). *Product Stewardship Guide: Overview and Implementation Guidance for this Important Aspect of Responsible Care*, Canadian Chemical Producers' Association, Ottawa.

Henderson, M. (1987). *Living with risk: the British Medical Association Guide*, Wiley for BMA, Chichester (ISBN 0-471-91598).

# 1 MDI, TDI and the polyurethane industry

MDI and TDI are high tonnage products, which comprise about 90 % of the total diisocyanate market. The predominant use of MDI and TDI is in the manufacture of polyurethanes. Polyurethanes are produced by reacting diisocyanates with polyols and other chemicals. The range of polyurethane types, from flexible or rigid lightweight foams to tough, stiff elastomers, allows them to be used in a wide diversity of consumer and industrial applications. Some examples are:

**Rigid foam**

- thermal insulation of buildings, refrigerators, deep freeze equipment, pipelines and storage tanks;
- buoyancy aids in boats and flotation equipment;
- packaging;
- furniture;
- equipment housings.

**Flexible foam**

- household furniture including bedding;
- automotive seating;
- cushioning for diverse industrial applications;
- textile laminates.

**Integral skin, semi-rigid and low density structural foams**

- steering wheels, headrests and other automotive interior trim components;
- furniture elements;
- sports goods such as skis and surf boards.

**Elastomers**

- shoe soles;
- vehicle body panels;
- rollers and gear wheels;
- conveyors;
- sealants for the construction and automotive industries;
- fibres.

Figure 1.1 shows the areas of application as a function of stiffness and density of each polyurethane product (Woods, 1990).

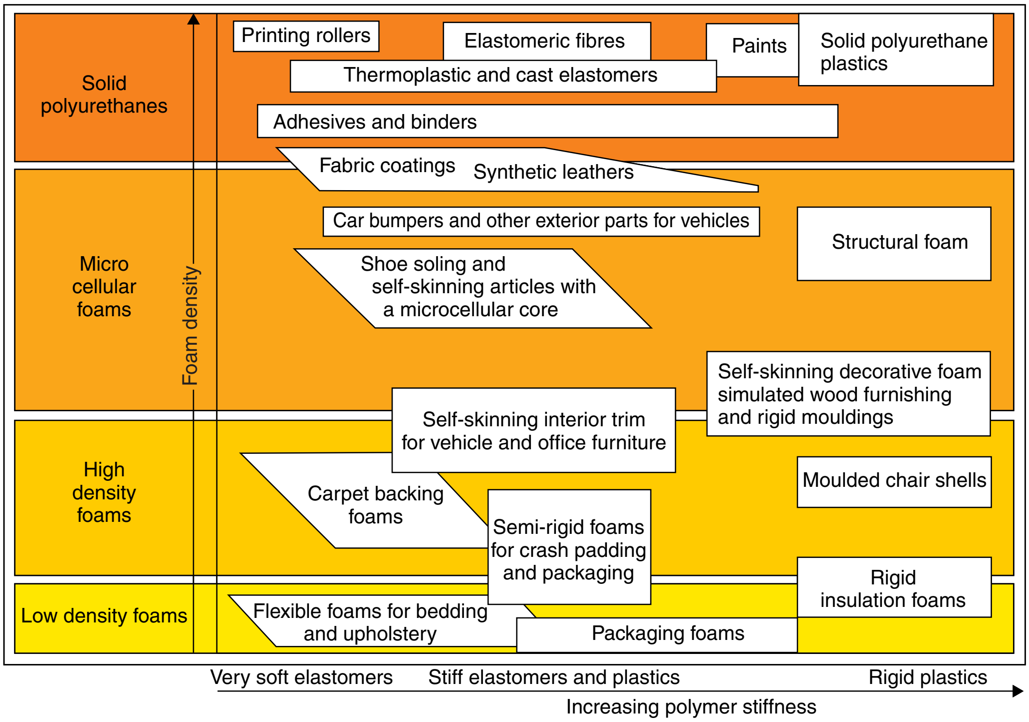


***Figure 1.1*** **Property matrix of polyurethanes (figure by courtesy of Huntsman Polyurethanes)**

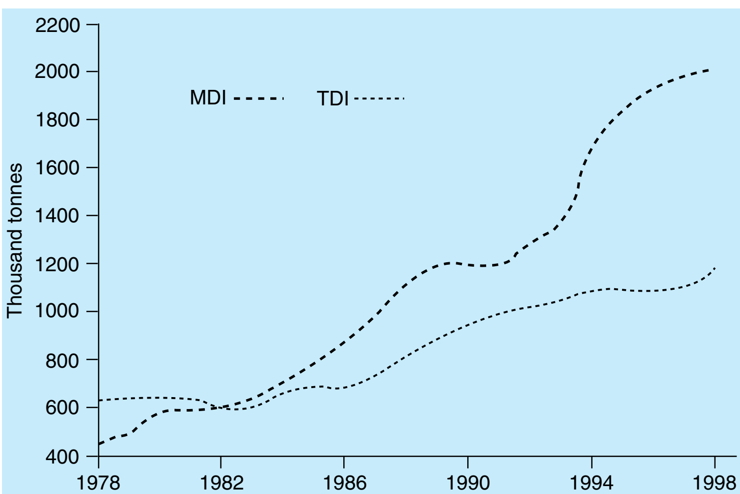


***Figure 1.2*** **Global tonnages of MDI and TDI from 1978 to 1998**

*References about MDI and TDI production levels*
CW (1998); Petersen (1999); ECN (1999); UT (2000).

By 2003 the global production of MDI and TDI together will approach 4 million tonnes. Over more than 40 years the tonnages of MDI and TDI have increased year upon year as new markets and new applications have been found (Figure 1.2). It is estimated that this growth trend is likely to continue at a high level as indicated by the statistics of market development around the world, especially in the Pacific Rim and in Latin America, and as there evolve high tonnage applications, such as the use of MDI as a particle board binder. Continuing vigilance in the safety of handling of MDI and TDI will be needed during this period of geographical and applicational expansion. The rapidly expanding product stewardship movement, in which MDI and TDI producers and the polyurethane industry have been collaborating closely for many years, will support this.

## Types of MDI

The acronym *MDI* was devised from one of the chemical's many names, *methylene diphenyl diisocyanate*. Common synonyms are diphenylmethane diisocyanate and diisocyanatodiphenylmethane. The generic term MDI is often used for pure MDI and for the technical grade of MDI commonly known as polymeric MDI. In Table 1.1 is given basic information about these types of MDI and modified MDIs, which can be made from both pure MDI and polymeric MDI.

***Table 1.1*** **Types of MDI used in industry.**

| Type of MDI | Description | Form at 25 °C |
|---|---|---|
| **MDI** | Generic term for any type of unmodified MDI. | – |
| **Polymeric MDI** | Comprises mixed monomeric MDI and higher molecular weight species. Formerly also called crude MDI or technical grade MDI. | Translucent brown liquid |
| **Pure MDI** | Commercial monomeric MDI. It is also known as monomeric MDI, 4,4′-MDI or MMDI. It comprises about 98 % 4,4′-MDI, with 2,4′- and 2,2′-MDI constituting most of the remainder. | White solid (fused or flake) |
| **Modified MDIs** also known as **MDI derivatives**. Some are known as **MDI prepolymers**. Others are known as **MDI variants**. | These terms represent either pure or polymeric MDI as modified to make handling easier or to increase the diversity of final polymer properties. Producers have wide ranges of products tailored to specific applications. | Whitish brown solids or liquids, depending on formulation |

The term *Polymeric MDI* is a misnomer: it is not a polymer. It is a liquid mixture containing monomeric MDI isomers and oligoisocyanates: the latter are sometimes referred as oligomers, which is incorrect usage. For certain applications it is necessary to refine the mixture by distillation and/or crystallization to form pure MDI, a solid at ambient temperature. Currently, the ratio of production levels of polymeric MDI to pure MDI that is manufactured is about 4:1. This ratio, and particularly the relative tonnages of modified MDIs

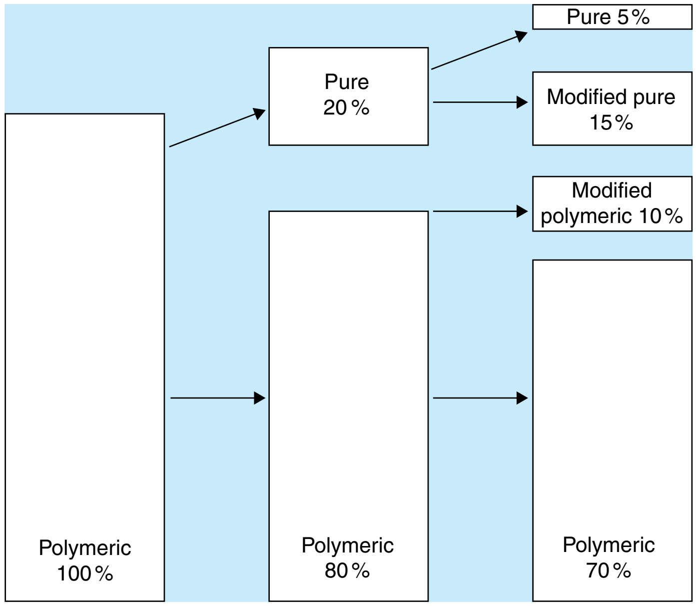


***Figure 1.3*** **Production of MDI types**

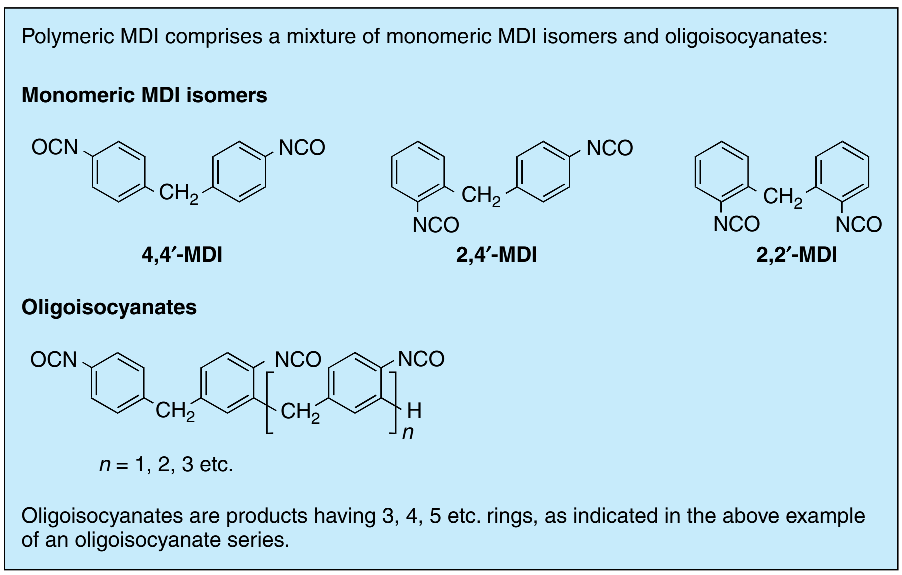


***Figure 1.4*** **Chemical structures of MDI species**

produced, will depend on the prevailing applications into which they are sold. A very approximate indication of the relative production levels of MDI types is shown in Figure 1.3.

Pure MDI is predominantly 4,4′-MDI monomer with a very small percentage of 2,4′-MDI and 2,2′-MDI isomers. Pure MDI is also known as monomeric MDI or as 4,4′-MDI (see Figure 1.4). Both pure MDI and polymeric MDI may be partially reacted to form modified MDIs, also called MDI derivatives, which include MDI variants and MDI prepolymers. There are solvent grades of some of these materials for applications which demand an even distribution of the diisocyanates. The pre-reacted types of MDI give improved chemical handling properties and allow more precise control of the nature of the polymer produced in the polyurethane reaction. For example, solid pure MDI can be partially reacted to form modified MDIs which are liquid at ambient temperatures. Conversion of pure MDI or polymeric MDI to the respective modified products is carried out by the original manufacturers or by specialist formulators. *Parts 5.1* and *5.2* give details of the manufacture and of the nomenclature of MDI, including structures and Chemical Abstract Registry numbers.

## Types of TDI

The mixture of TDI isomers contains at least 99 % monomeric TDI; there is no equivalent of polymeric MDI, which contains a range of higher molecular weight species.

The acronym *TDI* comes from several synonyms for TDI, the commonest of which is *toluene diisocyanate*: other widely used synonyms are toluylene diisocyanate and tolylene diisocyanate. TDI is produced as a single isomer, as mixtures of isomers (Figure 1.5) and as modified TDIs. In Table 1.2 are given the types of TDI used on an industrial scale. TDI is manufactured very predominantly as 80/20 TDI. The pure 2,4-TDI isomer is used in industrial quantities for special applications associated with elastomers. The pure 2,6-TDI isomer is synthesized only for use as a laboratory chemical.

There are two TDI isomers in industrial TDI mixtures:

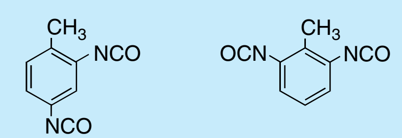


***Figure 1.5*** **Structures of TDI isomers**

***Table 1.2*** **Types of TDI used in industry.**

| Type of TDI | Description | Form at 25 °C |
|---|---|---|
| **TDI** | Generic term for all unmodified types of TDI. | – |
| **2,4-TDI** | An isomer produced in mixed isomers of TDI. | Colourless liquid |
| **80/20 TDI** | A mixture of 80 % 2,4-TDI with 20 % 2,6-TDI. Also known as 80:20 TDI. | Colourless liquid |
| **65/35 TDI** | A mixture of 65 % 2,4-TDI with 35 % 2,6-TDI. Also known as 65:35 TDI. | Colourless liquid |
| **Modified TDIs** Some are **TDI prepolymers** | Isomers of TDI which are partially reacted to give versatility in handling or in final polymer properties. | Colourless liquids |

## Test substances

Ultimately, it is important to understand how MDI and TDI interact with humans, with other species and with the physical environment. An extensive range of studies has been undertaken, largely by industry. However, there are limitations to the types of real life study which can be undertaken, both for ethical reasons and because of the complexity of the situations. Accordingly, many of the studies have been completed in research laboratories. One example is the study of laboratory biological systems to predict the effect of diisocyanates on humans. Another example is the use of precisely controlled laboratory pond studies to investigate the possible effects of diisocyanates in standing water such as canals and lakes. The choice of test substance for such research studies is important. Both MDI and TDI are hydrophobic and insoluble in water. In some cases solvents such as dimethylsulphoxide or dimethylformamide have been used to introduce MDI and TDI into water. The use of such solvents, which does not represent real-life situations, may give misleading results.

Of the various types of MDI, only polymeric MDI has been used widely as a test substance: pure MDI is unsuitable for many types of study because it is a waxy solid, which cannot be dispersed finely in water. Modified MDIs have not been reported widely as test substances because there are many proprietary variations and they are often reformulated. The individual solid isomers, 2,2′-MDI and 2,4′-MDI, have rarely been used as test substances in biological studies. The individual oligoisocyanates of MDI are very difficult to isolate and have not been used in studies. Even when polymeric MDI is used as a laboratory test substance there are problems in mixing it with water or aqueous biological systems.

Most studies of the effects of TDI have been carried out with the predominant commercial product, 80/20 TDI. However, individual isomers can be isolated readily and studies have also been carried out with 2,6-TDI as well as with the commercial 2,4-TDI and 65/35 TDI. All of these isomers and isomer mixtures are liquids under most test conditions. Where researchers fail to specify precisely what type of TDI has been employed, it is usually assumed that they have used 80/20 TDI.

### Diisocyanates and amines

It is important to recognize that MDI or TDI or related species may be converted very easily to the diamines MDA and TDA in some test systems or in analytical work-up procedures, especially when solvents are used. This can give rise to misleading results, since the chemical and biochemical reactions of the diisocyanates and diamines differ considerably. Examples of this have arisen with TDI in the Ames Test (Gahlmann *et al*., 1993; Seel *et al*., 1999) and in the analysis of airborne TDI using solvents in impingers (Nutt *et al*., 1979).

## Misapprehensions

Misinformed commentators on the safety, health and environmental scenes commonly make mistakes because of a similarity of sound of chemical terms or similarity of chemical structure. The following are corrections of common errors:

**Diisocyanates are *not* cyanides**

Although the two chemical names are similar, no cyanide is used to make isocyanates or is present in isocyanate products. In addition, no cyanide is released during the normal use of isocyanate-based polyurethane products. As with any nitrogen-containing organic substance (for example wood and some fabrics), polyurethanes liberate hydrogen cyanide under some burning conditions.

**MDI is *not* methyl isocyanate**

One particularly important misconception is that MDI is methyl isocyanate (MIC), the substance released in Bhopal, India, in 1984. The chemical structures, as well as the physical and toxicological effects of the two substances differ very considerably. MIC is highly volatile, whereas MDI has very low volatility. The ratio *MIC volatility: MDI volatility* at ambient temperature is approximately 35 000 000:1. MIC can form a blanket of dense, high concentration vapour, affecting a large area, as it did in Bhopal. This cannot arise with MDI because it is of such low volatility that MDI-saturated air has almost exactly the same density as air over a wide temperature range.

**Diisocyanates are *not* isothiocyanates**

There is occasional confusion between these two types of compound, which are quite different in their chemistry and biochemistry. Health problems associated with crops such as rape seed have been associated with the naturally occurring isothiocyanates, which are characterized by the –NCS group. Diisocyanates, which have reactive –NCO groups, are not naturally occurring.

**'Urethane' (ethyl carbamate) is *not* polyurethane**

Polyurethane is not a polymer of urethane (urethan), as might be expected from its name. Urethane is a chemical, also known as ethyl carbamate ($NH_2COOC_2H_5$), of molecular weight 89 and is an animal carcinogen. Polyurethanes are polymers of high molecular weight, which are biochemically inert. Urethane and polyurethanes differ very significantly in their chemistry and biochemistry.

## Polyurethanes made from MDI and TDI

MDI and TDI are used almost entirely for the production of polyurethane polymers. Accordingly, most references to the *use* of MDI and TDI in this book are related to polyurethane production. In 1998 the global tonnage of polyurethanes was 7.5 million tonnes. It is expected that about 10 million tonnes of polyurethanes per annum will be manufactured by 2002. At that time production levels for Americas, Europe and Asia Pacific will all be about the same (Petersen, 1999).

Polyurethane is sometimes abbreviated to *PU* or *PUR*. A further term, *PIR*, is commonly used for polyisocyanurates which are diisocyanate-based products with high thermal stability. The information given on diisocyanates in this book is, however, equally relevant both to polyurethane and to polyisocyanurate production.

## Production and usage of polyurethanes

### *Production based on region*

Figure 1.6 shows regional production of polyurethanes in 1998. Regions of high growth are Asia Pacific, which already has a very high per capita usage of polyurethanes, and Latin America.

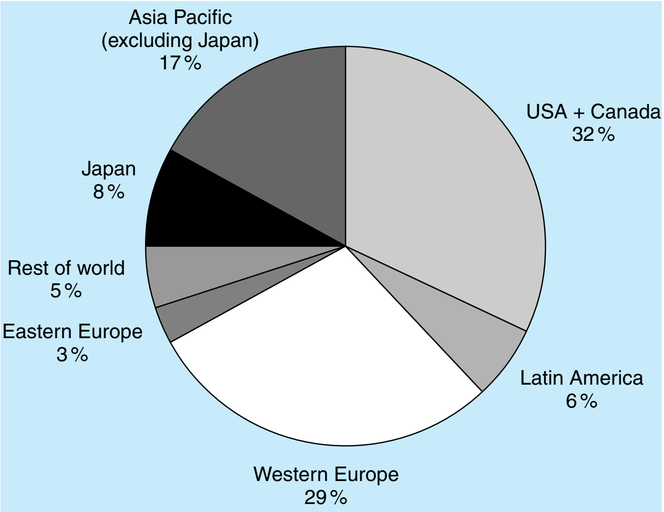


***Figure 1.6*** **Regional production of polyurethanes**

### *Production based on application*

Figure 1.7 shows percentage consumption of polyurethanes in 1998 according to the type of application. Furniture, mattresses and automotive seating are made predominantly from flexible foams and semi-rigid foams. Shoe applications relate to elastomers; construction and insulation are of rigid foams. Other applications include coatings, adhesives, artificial leather, fibres, and electronic applications.

### *Production based on types of polyurethane*

In Figure 1.8 is given a breakdown of polyurethane usage in 1998 according to types of polyurethane. Furniture applications are predominantly related to TDI-based flexible foams. Insulation and construction are almost entirely related to MDI-based rigid foams, and footwear is largely modified MDI-based

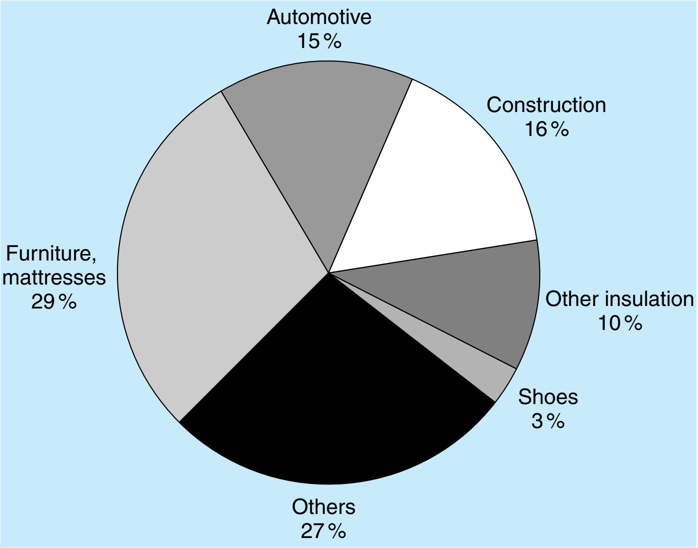


***Figure 1.7*** **Polyurethane production based on application**

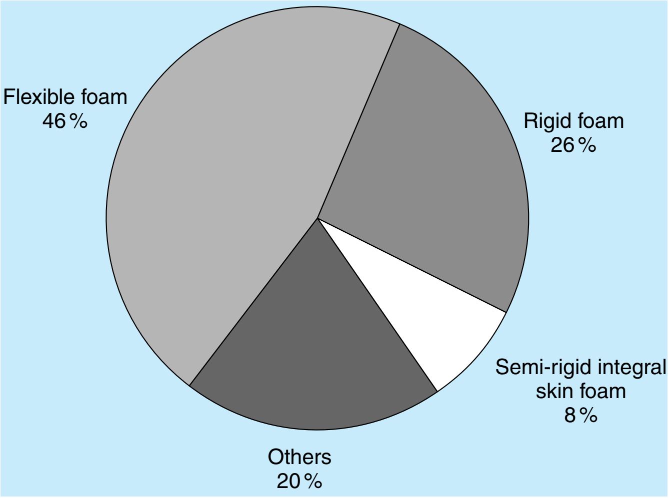


***Figure 1.8*** **Polyurethane production based on type of polyurethane**

elastomers. The large sector of other applications comprises a very wide diversity including elastomers, thermoplastic polyurethanes, wood products (e.g. particle board) and coatings. The automotive sector includes rigid body parts, seating, interior trim and paints.

## The components of polyurethanes

The basic reaction between a diisocyanate and a polyol produces a polyurethane addition polymer with the liberation of heat.

$$\text{diisocyanate} + \text{polyol} \longrightarrow \text{polyurethane polymer} + \text{heat}$$

Details of the chemistry of the reactions are given in *Part 5.3.*

However, a number of ancillary chemicals and processing aids are usually required to allow sufficient control to produce useful commercial products. Catalysts are needed to allow the reaction to progress at a speed compatible with production processes. Surfactants are used to control the interaction between nonhomogeneous components of the reacting system. The properties of the polymer structures may be modified by the use of chain extenders or by cross-linkers. Fire retardants, fillers and pigments may also be added.

Blowing agents can be added to the reacting systems to cause foaming. Blowing agents may be nonreactive or reactive. Nonreactive blowing agents act by evaporating within the foaming mix. Water, a reactive agent, causes blowing by reacting with MDI or TDI to form carbon dioxide gas within the polyurethane reaction mixture. According to the type of blowing agent and the concentration in the reacting mix, it is possible to produce polyurethane polymers of different densities, and of different thicknesses of skin. Water and other blowing agents are used together in formulations to achieve the required balance of density and physical properties. In Table 1.3 is given a list of typical components of polyurethane formulations. The most important reactant with MDI or TDI is the polyol, as indicated above.

## Polyurethanes: thermosets and thermoplastics

### *Thermosets*

Polyurethanes are produced predominantly as thermosets. This means that once the reactions have ceased the polyurethane is cured and it cannot be heat-shaped without degradation. This thermal stability results from the degree of cross-linking of polymer chains (the cross-link density) and/or the nature and frequency of repeating units within the polymer chains.

### *Thermoplastics*

A wide range of formulations may be used to produce thermoplastic polyurethanes (TPUs), based on pure MDI or modified MDI. TPUs are normally supplied in the form of pellets as feedstock for the production of polyurethane components. Unlike thermosetting materials, these can be thermoformed, usually by high temperature injection moulding or extrusion. The market for thermoplastic polyurethanes includes high performance footwear such as ski boots, automotive parts such as high performance elastomeric components, and hoses and electrical cabling.

## Processing of MDI and TDI to form polyurethanes

The versatility of polyurethanes is such that they are manufactured not only with a wide diversity of properties and forms, but also in a range of production situations from small workshops through to highly automated production lines. It must be emphasized that whatever degree of automation is used chemical reactions are being carried out in a factory with a workforce which has very largely not received an education in chemistry. Therefore a sound education in safety procedures is essential. Some processes for manufacturing polyurethanes are listed below:

***Table 1.3*** **Typical components of polyurethane formulations.**

| **Chemical type** | **Reactivity to diisocyanates** | **Example** |
|---|---|---|
| Polyol | Reactive | • Hydroxyl-terminated reaction products of ethylene oxide and propylene oxide, with an initiator such as glycerol |
| Chain extender | Reactive | • Bifunctional short chain reactive molecules such as butane diol |
| Cross-linker | Reactive | • Polyfunctional low molecular weight amines or alcohols such as triethanolamine |
| Blowing agent[a] | Reactive | • Water (producing carbon dioxide from the isocyanate–water reaction) |
| | Nonreactive | • Carbon dioxide (as gas or liquid) |
| | Nonreactive | • Pentane |
| | Nonreactive | • Methylene chloride |
| Catalyst | Reactive | • Hydroxyl-terminated tertiary aliphatic amines such as triethanolamine |
| | Nonreactive | • Tertiary aliphatic amines such as dimethyl cyclohexylamine, diazabicyclooctane, *N*-ethyl morpholine |
| | Nonreactive | • Stannous octoate |
| | Nonreactive | • Dibutyl tin dilaurate |
| Surfactant | Nonreactive | • Silicone liquids |
| Fire retardant | Nonreactive | • Tris(beta-chloropropyl) phosphate (TCPP) |
| | Reactive | • Propoxy brominated bisphenol A |
| Filler | Usually nonreactive | • Glass fibre |
| | Nonreactive | • Calcium carbonate |
| | Reactive, but insoluble | • Melamine |

[a]Formerly, CFCs were used very widely, but have now been replaced by other materials: see *Part 2, Releases to atmosphere from polyurethane manufacturing sites.*

- continuous foaming of slabstock for making blocks of rigid or flexible foam;
- reaction moulding of items such as car seating cushions or vehicle panels;
- spraying of insulation or paints;
- continuous production of polyurethane insulation board with metal or paper facings.

There are different ways in which the chemicals used to make polyurethanes are supplied and brought together during processing. MDI and TDI are almost invariably supplied without the incorporation of other polyurethane chemicals.

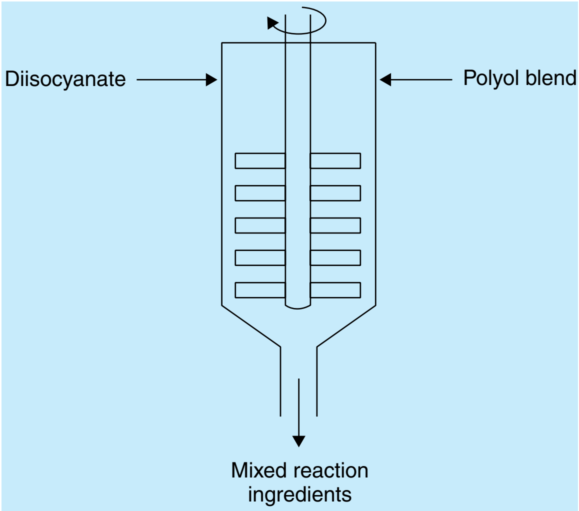


***Figure 1.9*** **Two-stream processing**

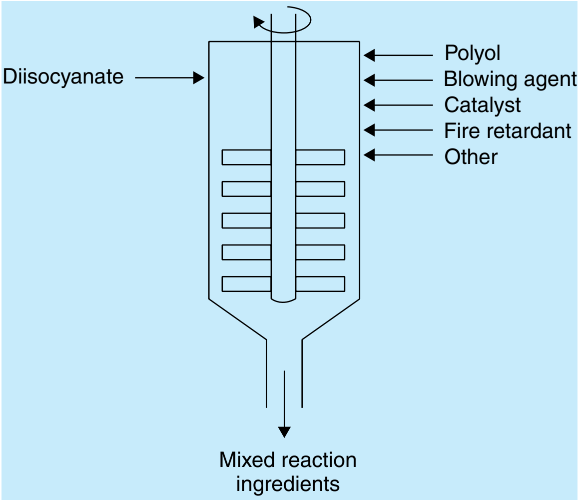


***Figure 1.10*** **Multi-stream processing**

This is because they react with many products, including water which is often found in polyurethane formulations. A polyurethane system may be supplied as two components, which are the diisocyanate and a complete blend of all the other materials. This allows processing with two-stream metering to the mixing head (see Figure 1.9). This approach is very simple, but inflexible as regards formulation and hence final product properties. It is appropriate for long production runs of the same polyurethane product.

The ultimate in flexibility is the individual supply and metering of each polyurethane component, using a multi-stream mixing head (see Figure 1.10). With this approach, variations in formulation can be used to produce polyurethanes of different specifications without interrupting continuous processes.

The formulation can even be changed during the dispensing of a shot of reacting mix into a mould. For example, composite cushioning with two hardness sectors can be produced in one shot.

### Non polyurethane applications of MDI and TDI

MDI and TDI may be used in processes without polyols, chain extenders or cross-linkers: however, the products are not polyurethanes. For example, MDI alone is used as a binder in particle board. In this process MDI and wood chips (or other substrate) are mixed and fed into a continuous hot press. The resulting board is bound as a result of the MDI reacting with the wood and with the water in the wood. Other examples of the use of MDI are as a binder in the production of sand-based foundry moulds and for the production of very low density polyurea foams for packaging. The precautions needed to handle MDI and TDI still apply to these non polyurethane processes.

## Reading

### References cited in the text

CW (1998). Product focus: MDI, *Chem. Week*, 8 Apr., 37.

ECN (1999). TDI, *Eur. Chem. News.*, **70**, 1–7 Feb., 18.

Gahlmann, R., Herbold, B., Ruckes, A. and Seel, K. (1993). Untersuchungen zur Stabilität aromatischer Diisocyanate in Dimethylsulfoxid (DMSO): Toluylendiisocyanate (TDI) und Diphenylmethandiisocyanat (MDI) im Ames-Test, *Zbl. Arbeitsmed.*, **43**, 34–38.

Nutt, A. R., Mapperley, B. W. and Skidmore, D. W. (1979). Toluenediamine (TDA) in polyurethane foam plant emissions. *Report No. CR 3093*. Dunlop Research Centre, Birmingham, UK.

Petersen, M. (1999). PU business set to grow. *Urethanes Technol.*, Jun./Jul., 12.

Seel, K., Walber, U., Herbold, B. and Kopp, R. (1999). Chemical behaviour of seven aromatic diisocyanates (toluenediisocyanates and diphenylmethanediisocyanates) under in vitro conditions in relationship to their results in the Salmonella/microsome test, *Mutat. Res.*, **438**, 109–123.

UT (2000). *Global Polyurethane Industry Directory 2001*, Urethanes Technology, Crain Communications, London.

Woods, G. (1990). *The ICI Polyurethanes Book*, 2nd edn., ICI Polyurethanes and Wiley, Everberg and Chichester (ISBN 0-471-92658-2).

### Further reading

Gum, W. F., Riese, W. and Ulrich, H. (1992). *Reaction Polymers: Polyurethanes, Epoxies, Unsaturated Polyesters, Phenolics, Special Monomers and Additives; Chemistry, Technology, Applications, Markets*, Carl Hanser Verlag, Munich (ISBN 3-446-15690-9).

Oertel, G. (1983). *Kunststoff Handbuch 7: Polyurethane*, 2nd edn., Carl Hanser Verlag, Munich (ISBN 3-446-13614-2).

Oertel, G. (1993). *Polyurethane Handbook: Chemistry–Raw materials–Processing–Application–Properties*, 2nd edn., Carl Hanser Verlag, Munich (ISBN 3-446-17198-3).

Uhlig, K. (1999). *Discovering Polyurethanes*, Carl Hanser Verlag, Munich (ISBN 3-446-21022-9).

Woods, G. (1990). *The ICI Polyurethanes Book*, 2nd edn., ICI Polyurethanes and Wiley, Everberg and Chichester (ISBN 0-471-92658-2).